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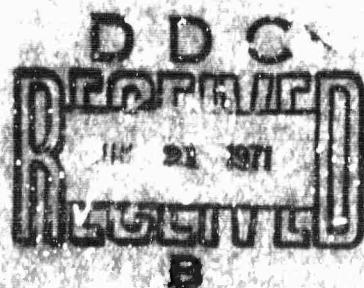
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4 P R O C E S S E S	LINK A		LINK B		LINK C	
	ROLE	WT	ROLE	WT	ROLE	WT
decay of correlations						
master equation						
stochastic processes						
Ursell functions						
reduced distribution functions						
reduced master equation						

DECAY OF CORRELATIONS IV. NECESSARY AND SUFFICIENT  
CONDITIONS FOR A RAPID DECAY OF CORRELATIONS

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## ABSTRACT

We consider  $N$  particle systems whose probability distributions obey the master equation. For these systems, we derive the necessary and sufficient conditions under which the reduced  $n$  particle ( $n < N$ ) probabilities also obey master equations and under which the Ursell functions decay to their equilibrium values faster than the probability distributions. These conditions impose restrictions on the form of the transition rate matrix and thus on the form of its eigenfunctions. We first consider systems in which the eigenfunctions of the  $N$  particle transition rate matrix are completely factorized and demonstrate that for such systems the reduced probabilities obey master equations and the Ursell functions decay rapidly if certain additional conditions are imposed. As an example of such a system we discuss a random walk of  $N$  pairwise interacting walkers. We then demonstrate that for systems whose  $N$  particle transition matrix can be written as a sum of one particle, two particle, etc. contributions, and for which the reduced probabilities obey master equations, the reduced master equations become in the thermodynamic limit those for independent particles, which have been discussed by us previously. As an example of such  $N$  particle systems we discuss the relaxation of a gas of interacting harmonic oscillators.

## 1. INTRODUCTION

In our previous papers in this series<sup>(1,2,3)</sup> (hereafter referred to as I, II, III, respectively) on the decay of correlations in various model systems, we have consistently found the relations:

$$P_n(\alpha^n; t) - P_n^{(0)}(\alpha^n) \sim P_1(\alpha; t) - P_1^{(0)}(\alpha); \quad n \geq 1 \quad (1.1)$$

$$R_n(\alpha^n; t) - R_n^{(0)}(\alpha^n) \sim [P_1(\alpha; t) - P_1^{(0)}(\alpha)]^n \quad (1.2)$$

where  $P_n(\alpha^n; t)$  stands for the  $n$ -particle distribution function at time  $t$  with dynamical variables  $\alpha^n = (\alpha_1, \alpha_2, \dots, \alpha_n)$ ;  $R_n(\alpha^n; t)$  stands for the  $n$ -particle relaxants<sup>(4)</sup> exemplified by the Ursell function,  $U_n$ , in papers I and II and the C-function in paper III;  $P_1$  denotes the one particle distribution function and the superscript zero denotes the equilibrium value. Equation (1.1) describes the asymptotic relaxation of the  $n$ -particle distribution functions to their equilibrium value  $P_n^{(0)}$  and Eq. (1.2) describes the asymptotic relaxation of the  $n$ -particle relaxant to its equilibrium value  $R_n^{(0)}$ . Equation (1.2) implies the important result that  $P_n(t)$ ,  $n > 1$ , relaxes to a functional of lower order distribution functions  $[P_{n-1}(t), P_{n-2}(t), \dots, P_1(t)]$  as  $[P_1(\alpha; t) - P_1^{(0)}(\alpha)]^n$ . These results hold for such diverse systems as non-interacting, initially correlated, particles in contact with a heat bath (I), an infinite chain of coupled harmonic oscillators (II), and the relaxation of spins in Glauber's<sup>(5)</sup> one-dimensional Ising model (III). It is evident that there must be an underlying physical basis for these identical results on the decay of correlations.

In this paper we study the general conditions under which the  $n$ -particle distribution functions and the Ursell functions will be of the form shown in Eqs. (1.1) and (1.2). We limit our consideration here to many body

systems whose time development is governed by a master equation as exemplified in papers I and III.

In Section 2 we develop eigenfunction expansions for the total probability  $P_N(t)$  and for the reduced probabilities  $P_n(t)$ ,  $n = 1, \dots, N-1$ . We derive the necessary and sufficient conditions on the form of the eigenfunctions and the master operator  $A_N$  under which the reduced probabilities obey master equations and under which the Ursell functions relax asymptotically to their equilibrium values faster than the reduced probability distributions relax to their equilibrium values.

In Section 3 we consider systems for which the eigenfunctions of  $A_N$  are completely factorized into single particle functions. We show that for such systems the reduced probabilities obey master equations and the Ursell functions decay more rapidly than the reduced probabilities.

In Section 4 we consider a model of  $N$  interacting random walkers as an example of a system for which the eigenfunctions of  $A_N$  are completely factorized. For the particular random walk chosen, in which the only transitions are those in which one particle takes a step to the right while another particle takes a step to the left,  $U_{N-n}$  decays asymptotically at the same rate as  $U_n$ . In the thermodynamic limit, the reduced master equations reduce to those for independent particles, and the asymptotic relaxation of  $U_n$  and  $P_n$  is again that found in Paper I, and given by Eqs. (1.1) and (1.2).

In Section 5 we generalize the results of Section 4 and demonstrate that for systems for which  $A_N$  can be written as a sum of one particle, two particle, etc. contributions, and for which the reduced probabilities obey master equations, the reduced master equations become in thermodynamic limit those for independent particles. As an example we consider in some detail a system of  $N$  interacting harmonic oscillators which undergo transitions as result of two body resonant collisions.

## 2. EIGENFUNCTION EXPANSIONS

We consider a system containing  $N$  particles and with a time dependent multivariate probability  $P_N(a^N; t)$ , where  $a^N = (a_1, a_2, \dots, a_N)$  where  $a_i$  is some property or set of properties of the  $i^{\text{th}}$  particle. We assume that the time dependence of  $P_N$  is governed by the master equation

$$\frac{\partial}{\partial t} P_N(a^N; t) = \sum_{\gamma^N} A_N(a^N, \gamma^N) P_N(\gamma^N; t) \quad (2.1)$$

where the transition rate  $A_N(a^N, \gamma^N)$  is related to the  $N$  particle "gain and loss" transition rates  $B_N(a^N, \gamma^N)$  by

$$A_N(a^N, \gamma^N) = B_N(a^N, \gamma^N) - \delta_{a^N, \gamma^N} \sum_{\mu^N} B_N(\mu^N, a^N) \quad (2.2)$$

Here and in the equations to follow  $\delta_{a^N, \gamma^N}$  is the Kronecker delta for discrete variables and the Dirac delta function for continuum variables. We shall write the solution to Eq. (2.1) in terms of eigenfunction expansions and investigate under what conditions the reduced probabilities  $P_n(a^n; t)$ ,  $n = 1, \dots, N-1$  obey master equations of the form

$$\frac{\partial}{\partial t} P_n(a^n; t) = \sum_{\gamma^n} A_n(a^n, \gamma^n) P_n(\gamma^n; t) \quad (2.3)$$

We shall also investigate the conditions under which the Ursell functions,  $U_n^{(1)}(a^n; t)$ , decay to their equilibrium value faster than the  $P_n(a^n; t)$  decay to their equilibrium values.

Equation (2.1) can be written in operator notation as

$$\frac{\partial}{\partial t} \underline{P}_N(t) = \underline{A}_N \underline{P}_N(t) \quad (2.4)$$

with the formal solution

$$P_N(t) = e^{\lambda_N t} \cdot P_N(0) \quad (2.5)$$

The right and left eigenfunction  $R_{N,\lambda_N}$  and  $L_{N,\lambda_N}$  of  $\lambda_N$  obey the equations

$$\lambda_N \cdot R_{N,\lambda_N} = \lambda_N R_{N,\lambda_N} \quad (2.6)$$

$$L_{N,\lambda_N} \cdot \lambda_N = \lambda_N L_{N,\lambda_N} \quad (2.7)$$

$$L_{N,\lambda_N} \cdot R_{N,\lambda_N} = \delta_{\lambda_N, \lambda_N} \quad (2.8)$$

where the  $\lambda_N$  are the eigenvalues, whose spectrum may be discrete and/or continuous. We consider here only systems for which the equilibrium distribution is unique, i.e.  $\lambda_N = 0$  is a nondegenerate eigenvalue. The other eigenvalues, however, may be degenerate and the eigenfunctions should have a label denoting the state as well as the eigenvalue. We shall suppress this label for ease of notation. Equation (2.8) is understood to imply that the eigenfunctions for different states are orthogonal. The probability  $P_N(t)$  can now be written

$$P_N(t) = \sum_{\lambda_N} e^{\lambda_N t} \left( L_{N,\lambda_N} \cdot P_N(0) \right) R_{N,\lambda_N} \quad (2.9)$$

where the symbol  $\sum$  denotes the sum over the discrete spectrum and the integral over the continuous spectrum of eigenvalues.

From detailed balance

$$\lambda_N(a^N, \gamma^N) P_N^{(o)}(\gamma^N) = \lambda_N(\gamma^N, a^N) P_N^{(o)}(a^N) \quad (2.10)$$

where

$$P_N^{(o)}(a^N) = P_N(a^N; \omega) \quad (2.11)$$

is the equilibrium probability distribution, and from the fact that  $\lambda_N$  is a

stochastic matrix, it follows that the eigenvalues  $\gamma_N$  are real and non-positive<sup>(6)</sup> and that

$$L_{N,\lambda_N}(a^N) = \left[ p_N^{(0)}(a^N) \right]^{-1} R_{N,\lambda_N}(a^N) \quad (2.12).$$

If  $\lambda_N = 0$  is part of the discrete spectrum

$$p_N^{(0)} = R_{N,0} \quad (2.13).$$

If  $\lambda_N = 0$  is part of the continuous spectrum

$$p_N^{(0)} = 0 \quad (2.14)$$

and in Eqs. (2.10) and (2.12)  $R_{N,0}$  should be used instead of  $p_N^{(0)}$ .

The reduced probabilities  $P_n(a^n; t)$ ,  $n = 1, \dots, N-1$ , for the  $n$  particles,  $i_1, \dots, i_n$ , are defined by

$$P_n(a^n; t) = \sum_{a^{N-n}} p_N(a^N; t) \quad (2.15)$$

where the sum is over the variables of the  $N-n$  other particles. It follows from Eq. (2.9) that

$$P_n(a^n; t) = \sum_{\lambda_N} e^{\lambda_N t} \left( L_{N,\lambda_N} \cdot p_N(0) \right) \sum_{a^{N-n}} R_{N,\lambda_N}(a^N) \quad (2.16).$$

We now investigate the conditions under which  $P_n(a^n; t)$  is a solution to Eq. (2.3), i.e. when  $p_n(t)$  is given by

$$p_n(t) = c^{A_n t} \cdot p_n(0) \quad (2.17)$$

or

$$P_n(a^n; t) = \sum_{\lambda_n} e^{\lambda_n t} \left( L_{n,\lambda_n} \cdot p_n(0) \right) R_{n,\lambda_n}(a^n) \quad (2.18)$$

where  $R_{n,\lambda_N}$  and  $L_{n,\lambda_N}$  are the right and left eigenfunctions, and  $\lambda_n$  the eigenvalues of  $\Delta_n$ . It is obvious that the  $\lambda_n$  must form a subset of the  $\lambda_N$ .

Clearly, Eq. (2.16) reduces to Eq. (2.18) if and only if, for each  $\lambda_N$ , either

$$i) \sum_{n=0}^N R_{n,\lambda_N}(a^N) = R_{n,\lambda_N}(a^n) = 0 \quad (2.19)$$

or

$$ii) (L_{n,\lambda_N} \cdot P_N(0)) = (L_{n,\lambda_N} \cdot P_n(0)) \quad (2.20)$$

Let us consider a  $\lambda_N$  for which Eq. (2.19) does not apply; for this  $\lambda_N$  Eq. (2.20) must apply and we can write

$$L_{n,\lambda_N}(a^N) = L_{n,\lambda_N}(a^n) \quad (2.21)$$

since Eq. (2.20) must be true for all  $P_N(0)$ . This subset of  $\lambda_N$  for which Eq. (2.21) applies is identical to the set of  $\lambda_n$ . It then follows from Eqs. (2.12), (2.13) and (2.21) that

$$R_{n,\lambda_N}(a^N) = \frac{R_{n,0}(a^N)}{R_{n,0}(a^n)} \cdot R_{n,\lambda_N}(a^n) \quad (2.22)$$

The physical significance of the fact that the reduced distribution functions obey the master equation, Eq. (2.3), is more readily understood from the condition that must be imposed on  $\Delta_N$ . This condition, which is of course equivalent to Eq. (2.21), is

$$A_n(a^n, \gamma^n) = \sum_{a^{N-n}} A_N(a^N, \gamma^N) \quad (2.23)$$

i.e. the transition rates for the n particle subsystem must be independent of the initial states of the other N-n particles. Equation (2.23) imposes severe restrictions on the properties of  $\Delta_N$  but these conditions are not severe

enough to determine uniquely its functional form. We discuss some sufficient conditions for Eq. (2.23) to hold in Section 3.

We now investigate the conditions on the eigenfunctions of the master operator under which the Ursell functions relax to their equilibrium form faster than the probability distributions relax to their equilibrium form. We start with the discussion of  $U_2$  and then extend our considerations to  $U_n$ . The two particle Ursell function is defined by

$$U_2(a_1, a_2; t) = P_2(a_1, a_2; t) - P_1(a_1; t) P_1(a_2; t) \quad (2.24)$$

with the property

$$\sum_{a_1} U_2(a_1, a_2; t) = \sum_{a_2} U_2(a_1, a_2; t) = 0 \quad (2.25).$$

The time dependence of  $U_2$  is given explicitly by

$$U_2(a_1, a_2; t) = \sum_{\lambda_N} e^{\lambda_N t} \left( \underline{L}_{N, \lambda_N} \cdot \underline{P}_N(0) \right) R_{2, \lambda_N}(a_1, a_2) - \sum_{\lambda_N, \lambda'_N} e^{(\lambda_N + \lambda'_N)t} \left( \underline{L}_{N, \lambda_N} \cdot \underline{P}_N(0) \right) \left( \underline{L}_{N, \lambda'_N} \cdot \underline{P}_N(0) \right) R_{1, \lambda_N}(a_1) R_{1, \lambda'_N}(a_2) \quad (2.26)$$

where we have used Eq. (2.16) and

$$R_{n, \lambda_N}(a^n) = \sum_{a^{N-n}} R_{N, \lambda_N}(a^N) \quad (2.27).$$

Equation (2.26) has the properties of Eq. (2.25) since

$$\sum_N R_{N, \lambda_N}(a^N) = \delta_{\lambda_N, 0} \quad (2.28)$$

which follows from Eqs. (2.8) and (2.12). If no restrictions are imposed on the eigenfunctions  $\underline{R}_{N, \lambda_N}$  the asymptotic decay of  $U_2$  is the same as the

asymptotic decay of  $\underline{P}_2$ , which is governed by  $\lambda_N^0$  which is the highest non zero eigenvalue for which  $R_{2,\lambda_N^0}$  is non zero. The asymptotic decay of  $\underline{P}_1$  will be the same as the asymptotic decay of  $\underline{P}_2$  if  $R_{1,\lambda_N^0}$  is non zero for the highest non zero eigenvalue; if  $R_{1,\lambda_N^0}$  is zero for this eigenvalue,  $\underline{P}_1$  will decay faster than  $\underline{P}_2$ .

In order for  $\underline{P}_2$  to decay faster than  $\underline{P}_2$  it is necessary that the coefficient of the term in Eq. (2.26) containing the highest non zero eigenvalue be zero for all initial conditions. This will be the case if and only if

$$R_{2,\lambda_N^0}(\alpha_1, \alpha_2) = R_{1,0}(\alpha_1)R_{1,\lambda_N^0}(\alpha_2) + R_{1,\lambda_N^0}(\alpha_1)R_{1,0}(\alpha_2) \quad (2.29)$$

for each eigenstate of  $\lambda_N^0$ .

The general expression for  $U_n$  is given by

$$\begin{aligned} U_n(\alpha^n; t) &\equiv \sum_{\xi} (-1)^k (k-1)! P_{m_1}(\alpha_{i_1}, \dots, \alpha_{i_{m_1}}; t) \dots P_{m_k}(\alpha_{i_{m-m_k+1}}, \dots, \alpha_{i_m}; t) \\ &= \sum_{\xi} (-1)^k (k-1)! \sum_{\lambda_N^{(1)}, \dots, \lambda_N^{(k)}} e^{\left(\lambda_N^{(1)} + \dots + \lambda_N^{(k)}\right)t} x \\ &\quad \prod_{j=1}^k \left( \underline{L}_{N,\lambda_N^{(j)}} \cdot \underline{P}_N^{(0)} \right) \left( \underline{R}_{m_j, \lambda_N^{(j)}}(\alpha_{i_1}, \dots, \alpha_{i_{m_j}}) \right) \end{aligned} \quad (2.30)$$

where the sum is over all partitions  $\xi$  of  $n$  particles in subgroups,  $k$  is the number of subgroups, and  $m_i$  the number of particles in the  $i^{\text{th}}$  subgroup. The  $n$  particle Ursell function has the important property

$$\sum_{\alpha_i} U_n(\alpha^n; t) = 0 \quad (2.31)$$

where the subscript  $i$  denotes any of the  $n$  particles. An extension of the argument of the last paragraph yields the result that the  $U_m$ ,  $m=2, \dots, n$ , decay asymptotically faster than  $\exp(\lambda_N^0 t)$  if and only if

$$R_{n, \lambda_N^0}(\alpha^n) = \sum_{j=1}^n R_{n-1, 0}(\alpha^{n-1}) R_{1, \lambda_N^0}(\alpha_i) \quad (2.32).$$

Note that in this case the time dependence of  $U_n$  is independent of whether or not the equilibrium probability distribution  $P_n^{(0)}$  factorizes into single particle functions.

If  $P_n(t)$ ,  $n=1, \dots, N-1$ , is a solution of the reduced master equation, Eq. (2.3), so that Eqs. (2.19) through (2.22) apply, the Ursell functions will not decay any faster than the probabilities unless additional assumptions are made. Sufficient additional assumptions are:

- i) The equilibrium distribution is factorized into single particle functions, i.e.

$$P_n^{(0)}(\alpha^n) = \prod_{i=1}^n P_i^{(0)}(\alpha_i) ; \quad (2.33)$$

- ii) The eigenfunction  $R_{1, \lambda_N^0}(\alpha_i) \neq 0$  for each of the eigenstates of  $\lambda_N^0$  for one of the particles of the set  $n$ .

Under these conditions it follows from Eq. (2.22) that for each eigenstate of  $\lambda_N^0$

$$R_{1, \lambda_N^0}(\alpha_j) = 0, \quad j \neq i \quad (2.34)$$

and thus Eq. (2.22) is identical with Eq. (2.32). Therefore  $U_m$ ,  $m=2, \dots, n$ , decays asymptotically faster than  $P_m$ ,  $m=1, \dots, n$ .

### 3. COMPLETELY FACTORIZED EIGENFUNCTIONS

As we have shown in the last section, the specification of the necessary conditions for the fast decay of the Ursell functions is quite complicated. In this section we shall consider some fairly stringent sufficient conditions for the fast decay of the Ursell functions and for the validity of the master equation for the reduced distribution functions, Eq. (2.3).

We assume that all of the eigenfunctions of the master operator  $\underline{A}_N$  are completely factorized into single particle functions, i.e.

$$R_{N,\lambda_N}(\alpha^N) = \prod_{i=1}^N R_{v_i}(\alpha_i) \quad (3.1)$$

where we use the notation

$$\lambda_N = \lambda_N(v_1, \dots, v_N) \equiv \lambda_N(v^N) \quad (3.2)$$

with  $\lambda_N(0, \dots, 0) = 0$ . Under these conditions Eq. (2.9) can be written

$$P_N(\alpha^N; t) = \sum_{v^N} e^{\lambda_N(v^N)t} \left( L_{N,\lambda_N} \cdot P_N(0) \right) \prod_{i=1}^N R_{v_i}(\alpha_i) \quad (3.3)$$

where

$$L_{N,\lambda_N}(\alpha^N) = \prod_{i=1}^N R_{v_i}(\alpha_i) / R_0(\alpha_i) = \prod_{i=1}^N L_{v_i}(\alpha_i) \quad (3.4)$$

and  $R_0(\alpha_i) = P_1^{(0)}(\alpha_i)$  is the one particle equilibrium distribution. Equation (3.4) follows from Eq. (2.12). The orthonormality condition, Eq. (2.8), is equivalent to

$$\sum_{\alpha_i} L_{v_i}(\alpha_i) R_{v_i}(\alpha_i) = \delta_{v_i, v_i} \quad (3.5)$$

If we take  $v_i = 0$  this yields

$$\sum_{\alpha_i} R_{v_i}(\alpha_i) = \delta_{0, v_i} \quad (3.6)$$

Equation (2.16) for the reduced probabilities  $\underline{p}_n$  now becomes

$$p_n(\alpha^n; t) = \sum_{v^n} e^{\lambda_N(v^n)t} \left( \underline{L}_{N, \lambda_N} \cdot \underline{p}_N(0) \right) \prod_{i=1}^n R_{v_i}(\alpha_i) \prod_{i=n+1}^N \delta_{0, v_i} \quad (3.7)$$

where we have used Eq. (3.6). The sum over  $v_{n+1}, \dots, v_N$  in Eq. (3.7) can be immediately performed to yield

$$p_n(\alpha^n; t) = \sum_{v^n} e^{\lambda_n(v^n)t} \left( \underline{L}_{n, \lambda_n} \cdot \underline{p}_n(0) \right) \prod_{i=1}^n R_{v_i}(\alpha_i) \quad (3.8)$$

where

$$\lambda_n(v^n) \equiv \lambda_N(v^n, 0, \dots, 0) \quad (3.9)$$

and

$$\underline{L}_{n, \lambda_n}(\alpha^n) = \prod_{i=1}^n \underline{L}_{v_i}(\alpha_i) \quad (3.10)$$

Equation (3.8) is obviously of the form of Eq. (2.18) and thus the reduced probability  $\underline{p}_n$  obeys the master equation, Eq. (2.3). Therefore the factorization of the eigenfunctions  $\underline{R}_{N, \lambda_N}$  as given in Eq. (3.1) is a sufficient condition for the validity of Eq. (2.3).

We shall now investigate the properties of the Ursell functions when all the eigenfunctions factorize. It follows from (3.8) and (3.10) that the terms in Eq. (3.8) for which  $v_j = 0$ ,  $j = 1, \dots, n$ , are of the form  $p_{n-1}(\alpha^{n-1}; t) p_1^{(0)}(\alpha_j)$ . Thus Eq. (3.8) can be rewritten

$$\begin{aligned} p_n(\alpha^n; t) &= \sum_m p_{n-m}(\alpha^{n-m}; t) p_m^{(0)}(\alpha^m) \\ &+ \sum_{v^n} e^{\lambda_n(v^n)t} \left( \underline{L}_{n, \lambda_n} \cdot \underline{p}_n(0) \right) \prod_{i=1}^n R_{v_i}(\alpha_i) \end{aligned} \quad (3.11)$$

where the sum over  $\eta$  is over all partitions of  $n$  particles into two subgroups where  $m$  goes from 1 to  $n$ . The notation  $\sum'_{\eta}$  implies the sum over all possible non-zero values of  $v_1, \dots, v_n$ . Substitution of Eq. (3.11) into Eq. (2.30) for  $\underline{U}_n(t)$  yields

$$\underline{U}_n(a^n; t) = \sum_{\xi} (-1)^k (k-1)! \sum'_{v^n} \exp \left( \lambda_{m_1}^{m_1} (v^1) + \dots + \lambda_{m_k}^{m_k} (v^k) \right) t$$
(3.12)

$$\times \prod_{i=1}^k \left( L_{m_i, \lambda_{m_i}} \cdot P_{m_i}(0) \right) \prod_{i=1}^n R_{v_i}(a_i)$$

where we have used the fact that factorized probabilities do not contribute to the Ursell functions. Note that because of the restriction on the sum over  $v^n$ , all the  $\lambda_{m_i}$  that appears in Eq. (3.12) are non zero. The asymptotic decay of  $\underline{U}_n$  is determined by the maximum value of  $\lambda_{m_1}^{m_1} (v^1) + \dots + \lambda_{m_k}^{m_k} (v^k)$ ,  $v_1, \dots, v_n \neq 0$ .

The stringent conditions on the eigenfunctions in Sections 2 and 3 for the rapid decay of the Ursell function  $\underline{U}_N(t)$  do not provide much physical insight. It would be preferable if these conditions could be stated in terms of properties of the operators  $A_N$  and  $A_n$  of the  $N$  particle and reduced  $n$  particle master equations. We have been unable to do that in general. In Sections 4 and 5 we present and discuss some sufficient conditions on the  $A_N$  and  $A_n$  for the rapid decay of correlations. These conditions do yield physical insight into the types of interactions which lead to a rapid decay of correlations in stochastic processes governed by a master equation.

#### 4. RANDOM WALK WITH INTERACTIONS

In this section we consider  $N$  pairwise interacting random walkers on a finite one-dimensional lattice with periodic boundary conditions. The sites on the lattice might represent, for example, the internal states of gas particles. The steps of the random walkers on the lattice mirrors the results of the binary collisions of the gas particles. The features of the problem which are of particular interest to us are the asymptotic decay of the Ursell functions and the structure of the transition rate matrix of the master equation in the thermodynamic limit.

We consider  $N$  random walkers with binary interactions on a finite one-dimensional lattice with  $\ell$  sites and periodic boundary conditions. The position of particle  $i$  on the lattice is denoted by  $m_i = 1, \dots, \ell$ ; with  $i = 1, \dots, N$ . In our model, any site  $m$  can be occupied by more than one particle subject to the restriction that the total number of particles equals  $N$ . We write the master equation of the  $N$  particle system as

$$\frac{\partial}{\partial t} P_N(m^N; t) = \frac{\alpha}{N} \sum_{\substack{i \neq j \\ 1}}^N \left[ P_N(m_1, \dots, m_{i-1}, \dots, m_j+1, \dots, m_N; t) - P_N(m^N; t) \right] \quad (4.1)$$

where  $\alpha$  is a constant transition rate for the transitions  $m_i \rightarrow m_{i-1}$ ;  $m_j \rightarrow m_j+1$ . This equation describes a system with two particle interactions such that one particle moves one step to the right while the other particle moves one step to the left while all other particles remain in the same state. In this model  $\sum_{i=1}^N m_i$  is conserved in the sense that for all states that occur in Eq. (4.1),

$$\sum_{i=1}^N m_i = C + k\ell \quad (4.2)$$

where  $C$  is a constant and  $k$  is an integer.

The eigenfunctions of the master operator are

$$R_{N, v^N} (m^N) = \lambda^{-N} \exp \left[ \frac{2\pi i}{\lambda} v^N m^N \right] \\ = \prod_{j=1}^N R_{v_j} (m_j) \quad , \quad v_j = 0, 1, \dots, \lambda-1, \quad (4.3)$$

where

$$R_{v_j} (m_j) = \lambda^{-1} \exp \frac{2\pi i}{\lambda} v_j m_j \quad (4.4).$$

The eigenvalues are

$$\lambda_N (v^N) = \frac{2\alpha}{N} \sum_{i < j}^N \left[ \cos \frac{2\pi}{\lambda} (v_i - v_j) - 1 \right] \quad (4.5).$$

It is clear that

$$\lambda_N (v^N) = 0$$

if and only if

$$v_k = v, \quad k=1, \dots, N \quad (4.6)$$

for all  $v_k = 0, \dots, \lambda-1$ . The zero eigenvalue  $\lambda_N$  is  $\lambda$  fold degenerate which is a consequence of the conservation law expressed in Eq. (4.2). The highest non-zero eigenvalue  $\lambda_N^*$  for  $P_N$  and  $U_N$  is

$$\lambda_N^* = \lambda_N (v+1, v, v, \dots, v) = \frac{2\alpha}{N} (N-1) \left( \cos \frac{2\pi}{\lambda} - 1 \right) = -\Lambda \quad (4.7).$$

The  $N$  particle eigenfunctions in this model are completely factorized into one particle functions and thus we are dealing with a special case of the systems discussed in Section 3. The reduced probabilities  $P_n$  obey master equations of the form of Eq. (2.3). The reduced eigenfunctions are given by

$$R_{n,v^n}(m^n) = \prod_{j=1}^n R_{v_j}(m_j) \quad (4.8)$$

and the reduced eigenvalues are

$$\begin{aligned} \lambda_n(v^n) &= \lambda_N(v^n, 0, \dots, 0) \\ &= \frac{2\alpha(N-n)}{N} \sum_{j=1}^n \left[ \cos \frac{2\pi}{k} v_j - 1 \right] + \frac{2\alpha}{N} \sum_{\substack{i < j \\ 1}}^n \left[ \cos \frac{2\pi}{k} (v_i - v_j) - 1 \right] \end{aligned} \quad (4.9)$$

It should be noted that

$$\lambda_n(v^n) = 0; \quad n=1, \dots, N-1 \quad (4.10)$$

if and only if

$$v_k = 0, \quad k = 1, 2, \dots, n \quad (4.11)$$

Thus the zero eigenvalue for all reduced probabilities is non degenerate.

The highest non-zero eigenvalue  $\lambda_n^*$  for  $P_n(m^n)$  is

$$\lambda_n^* = \lambda_n(1, 0, \dots, 0) = \frac{2\alpha}{N} (N-1) \left( \cos \frac{2\pi}{k} - 1 \right) = -\Lambda \quad (4.12)$$

and thus all the reduced probabilities decay asymptotically to their equilibrium values as

$$P_n(m^n; t) - P_n^{(0)}(m^n) \sim c_n e^{-\Lambda t} \quad (4.13)$$

where  $c_n$  is a constant which depends on the initial conditions and where

$$P_n^{(0)}(m^n) = \ell^{-n} \quad (4.14)$$

The expression for  $U_n(m^n; t)$  is given in Eq. (3.12). The highest non-zero eigenvalue appearing in this expression is

$$\lambda_n(1,1,\dots,1) = \frac{2\pi(N-n)}{N} (\cos \frac{2\pi}{\ell} - 1) = -\frac{N-n}{N-1} n\Lambda \quad (4.15)$$

for  $n=1,\dots,N-1$ . Thus,  $U_n(m^n; t)$ ,  $n=2,\dots,N-1$ , decays asymptotically to its equilibrium value  $U_n^{(0)} = 0$  as

$$U_n(m^n; t) \sim c'_n e^{-\frac{n(N-n)}{N-1} \Lambda t} \quad (4.16)$$

where  $c'_n$  is a constant which depends on the initial condition. Note that

$$U_1(m; t) = P_1(m; t).$$

From the form of  $\lambda_N^{(0)}$  in Eq. (4.7) it follows that the  $N$ -particle functions  $P_N(t)$  and  $U_N(t)$  decay asymptotically to their equilibrium forms as

$$P_N(t) - P_N^{(0)} \sim c_N e^{-\Lambda t} \quad (4.17)$$

and

$$U_N(t) - U_N^{(0)} \sim c'_N e^{-\Lambda t} \quad (4.18)$$

where

$$U_N^{(0)} = P_N^{(0)} - \ell^{-N} \quad (4.19)$$

and  $P_N^{(0)}$  depends on the initial conditions because of the degenerate zero eigenvalue as given in Eq. (4.6).

We now discuss the behavior of the Ursell functions  $U_n(t)$  for finite  $N$  and in the thermodynamic limit as  $N \rightarrow \infty$ . For  $N$  finite,  $U_{N-n}(t)$  decays asymptotically at the same rate as  $U_n(t)$ , which follows immediately from Eq. (4.16). The fastest decaying Ursell functions are those for which  $n \approx \frac{N}{2}$ . The slowest decaying Ursell functions are those with  $n \ll N$  and  $n \approx N$ . The Ursell functions for  $n \approx N$  decay slowly owing to the conservation law given in Eq. (4.2). In the thermodynamic limit, the asymptotic decay of the

reduced probabilities  $\underline{p}_n(t)$  is still given by Eq. (4.13) while the decay of the Ursell functions  $\underline{U}_n(t)$  is given by

$$\underline{U}_n(t) \sim c'_n e^{-n\lambda t} \quad (4.20)$$

which follows from Eq. (4.16). In the thermodynamic limit, our model systems thus has the identical asymptotic behavior for  $\underline{p}_n(t)$  and  $\underline{U}_n(t)$  as previously found in I and II.

The following question immediately arises: why does this model system with interactions behave, in the thermodynamic limit, in the same way as the independent particle systems considered in I? The operator  $\underline{A}_N$  in the master equation (4.1) can be written as

$$\underline{A}_N(m^N, q^N) = \frac{\alpha}{N} \sum_{i \neq j}^N \left\{ \left[ \delta_{m_i-1, q_i} \delta_{m_j+1, q_j} \prod_{k \neq i, j}^N \delta_{m_k, q_k} \right] - \delta_{m^N, q^N} \right\} \quad (4.21).$$

The operator  $\underline{A}_n$  for the reduced master equation is

$$\begin{aligned} \underline{A}_n(m^n, q^n) &= \frac{\alpha}{N} \sum_{i \neq j}^n \left\{ \left[ \delta_{m_i-1, q_i} \delta_{m_j+1, q_j} \prod_{k \neq i, j}^n \delta_{m_k, q_k} \right] - \delta_{m^n, q^n} \right\} \\ &+ \frac{\alpha(N-n)}{N} \sum_{i=1}^n \left\{ \left[ \left( \delta_{m_k-1, q_i} + \delta_{m_k+1, q_i} \right) \prod_{k \neq i}^n \delta_{m_k, q_k} \right] - 2\delta_{m^n, q^n} \right\} \end{aligned} \quad (4.22).$$

In the thermodynamic limit,  $\underline{A}_n$  becomes

$$\underline{A}_n(m^n, q^n) = \alpha \sum_{i=1}^n \left[ \delta_{m_i-1, q_i} + \delta_{m_i+1, q_i} - 2\delta_{m_i, q_i} \right] \prod_{k \neq i}^n \delta_{m_k, q_k} \quad (4.23).$$

Thus, in the thermodynamic limit, the  $n$ -particle transition rate  $\Lambda_n$  is the sum of single particle transition rates and is identical in form to Eq. (2.15) of Paper I for independent particle dynamics.

## 5. MASTER EQUATION MODELS FOR INTERACTING GASES

In this section we consider systems containing  $N$  identical interacting particles in which the operator  $\underline{\Lambda}_N$  for an  $N$  particle master equation can be written as a sum of one particle, two particle, etc. contributions. We show that in the thermodynamic limit as  $N \rightarrow \infty$ , the reduced master equation operators  $\underline{\Lambda}_n$  can be written as a sum of one particle terms as long as Eq. (2.23) applies. We illustrate our discussion by treating a system of  $N$  interacting harmonic oscillators.

We consider an  $N$ -particle transition rate matrix of the form

$$\begin{aligned}
 \underline{\Lambda}_N(a^N, \gamma^N) = & \sum_{i=1}^N \underline{\Lambda}_1^{(1)}(a_i; \gamma_i) \prod_{\substack{k \neq i \\ 1}}^N \delta_{a_k, \gamma_k} + \\
 & \frac{1}{2N} \sum_{\substack{i \neq j \\ 1}}^N \underline{\Lambda}_2^{(2)}(a_i, a_j; \gamma_i, \gamma_j) \prod_{\substack{k \neq i, j \\ 1}}^N \delta_{a_k, \gamma_k} + \\
 & \frac{1}{6N^2} \sum_{\substack{i \neq j \neq \ell \\ 1}}^N \underline{\Lambda}_3^{(3)}(a_i, a_j, a_\ell; \gamma_i, \gamma_j, \gamma_\ell) \prod_{\substack{k \neq i, j, \ell \\ 1}}^N \delta_{a_k, \gamma_k} + \dots
 \end{aligned} \tag{5.1}$$

where  $\underline{\Lambda}_2^{(2)}$ ,  $\underline{\Lambda}_3^{(3)}$ , etc. are symmetric when the particle indices are permuted. Here  $\underline{\Lambda}_1^{(1)}$  is a one particle transition rate matrix which has the property

$$\sum_{a_i} \underline{\Lambda}_1^{(1)}(a_i; \gamma_i) = 0 ; \tag{5.2}$$

$\underline{\Lambda}_2^{(2)}$  is a two particle transition rate matrix with the property

$$\sum_{a_i, a_j} \underline{\Lambda}_2^{(2)}(a_i, a_j; \gamma_i, \gamma_j) = 0 ; \tag{5.3}$$

$\underline{\Lambda}_3^{(3)}$  is a three particle transition rate matrix with the property

$$\sum_{\alpha_i, \alpha_j, \alpha_\ell} A_3^{(3)}(\alpha_i, \alpha_j, \alpha_\ell; \gamma_i, \gamma_j, \gamma_\ell) = 0 \quad : \quad (5.4)$$

etc. The form of  $\underline{A}_N$  in Eq. (5.1) implies that the systems under consideration can be described in terms of one particle, two particle, three particle, etc. interactions as is the case, for instance, for weakly interacting systems with short range forces. The factors  $N^{-(i-1)}$  in front of the sums take account of the frequencies of  $i$ -particle collisions. Thus, the  $A_i$  are independent of  $N$ . We assume that for the operator  $\underline{A}_N$  given in Eq. (5.1), the condition (2.23) holds in the thermodynamic limit as  $N \rightarrow \infty$ . In this case,  $A_n$  will be given by

$$A_n(\alpha^n; \gamma^n) = \sum_{i=1}^n A_1(\alpha_i; \gamma_i) \prod_{\substack{k \neq i \\ k=1}}^n \delta_{\alpha_k, \gamma_k} \quad (5.5)$$

where

$$\underline{A}_1 = \underline{A}^{(1)} + \underline{A}^{(2)} + \underline{A}^{(3)} + \dots \quad (5.6)$$

and where

$$A^{(1)}(\alpha_i; \gamma_i) = A_1^{(1)}(\alpha_i; \gamma_i) \quad (5.7)$$

$$A^{(2)}(\alpha_i, \gamma_i) = \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{j=1}^N \sum_{\alpha_j} A_2^{(2)}(\alpha_i, \alpha_j; \gamma_i, \gamma_j) \quad (5.8)$$

$$A^{(3)}(\alpha_i, \gamma_i) = \lim_{N \rightarrow \infty} \frac{1}{N^2} \sum_{j, \ell=1}^N \sum_{\alpha_j} \sum_{\alpha_\ell} A_3^{(3)}(\alpha_i, \alpha_j, \alpha_\ell; \gamma_i, \gamma_j, \gamma_\ell) \quad (5.9)$$

etc. In writing Eqs. (5.8) and (5.9) we have assumed that the two particle, three particle, etc. contributions to  $\underline{A}_N$  obey the condition (2.23) in the thermodynamic limit. In many systems  $\sum_{\alpha_j} A_2^{(2)}(\alpha_i, \alpha_j; \gamma_i, \gamma_j)$  will be independent

of  $\gamma_j$ ; in other systems, as we shall see below, it is necessary to take the sum over  $j$  to obtain a quantity independent of  $\gamma_j$  in thermodynamic limit.

Note that if  $A_n$  has the form given in Eq. (5.5), the results given in I for independent particle systems will again apply.

We now consider the example of a gas of interacting harmonic oscillators which exchange only vibrational energy. The  $N$  particle master equation has the form<sup>(7)</sup>

$$\frac{\partial}{\partial t} P_N(m^N; t) = \sum_{q^N} A_N(m^N, q^N) P_N(q^N; t) =$$

$$\frac{a}{N} \sum_{\substack{i \neq j \\ 1}}^N \left[ m_i(m_j+1) P_N(m_1, \dots, m_i-1, \dots, m_j+1, \dots, m_N; t) - \right. \\ \left. (m_i+1 m_j) P_N(m^N; t) \right] \quad (5.10)$$

where  $a$  is a rate coefficient and where  $m_i=0, 1, \dots$  with  $i=1, \dots, N$ , denotes the states of the  $i^{\text{th}}$  oscillator with energy  $E(m_i) = m_i \hbar \omega$ . The dimensionless mean vibrational energy per particle,  $\epsilon$  is given by

$$\epsilon = \frac{1}{N \hbar \omega} \sum_{m_i} E(m_i) = \frac{1}{N} \sum_{m_i=1}^N m_i \quad (5.11).$$

Clearly, this mean energy is a constant which is conserved during the relaxation process. In order for the relaxation process to take place on the constant energy shell with energy  $N\epsilon$  it is necessary to choose initial conditions such that  $P_N(m^N; 0)$  is non-zero only when  $\sum m_i = N\epsilon$ . The  $N$ -particle master operator has the form

$$A_N(m^N; q^N) = \frac{1}{2N} \sum_{\substack{i \neq j \\ 1}}^N A_2^{(2)}(m_i, m_j; q_i, q_j) \prod_{\substack{k=1 \\ k \neq i, j}}^N \delta_{m_k, q_k} \quad (5.12)$$

where

$$\begin{aligned}
A_2^{(2)}(m_i, m_j; q_i, q_j) &= a \left\{ m_i(m_j+1) \delta_{m_i-1, q_i} \delta_{m_j+1, q_j} \right. \\
&\quad \left. + (m_i+1) m_j \delta_{m_i+1, q_i} \delta_{m_j-1, q_j} - [(m_i+1) m_j + m_i(m_j+1)] \delta_{m_i, q_i} \delta_{m_j, q_j} \right\}
\end{aligned} \tag{5.13}$$

Equation (5.12) is clearly a special case of Eq. (5.1). The two particle transition rate matrix  $\underline{A}_2^{(2)}$  has the properties

$$\begin{aligned}
C(m_i; q_i, q_j) &\equiv \sum_{m_j} A_2^{(2)}(m_i, m_j; q_i, q_j) = \\
&= a q_j \left\{ m_i \delta_{m_i-1, q_i} + (m_i+1) \delta_{m_i+1, q_i} - (2m_i+1) \delta_{m_i, q_i} \right\} \\
&\quad + a \left\{ (m_i+1) \delta_{m_i+1, q_i} - m_i \delta_{m_i, q_i} \right\}
\end{aligned} \tag{5.14}$$

and

$$\begin{aligned}
A^{(2)}(m_i; q_i) &= \lim_{N \rightarrow \infty} \frac{1}{N} \sum_{\substack{j=1 \\ j \neq i}}^N C(m_i; q_i, q_j) = \\
&= a \left\{ \epsilon m_i \delta_{m_i-1, q_i} + (\epsilon+1) (m_i+1) \delta_{m_i+1, q_i} - (2\epsilon m_i + \epsilon + m_i) \delta_{m_i, q_i} \right\}
\end{aligned} \tag{5.15}$$

where the limit  $N \rightarrow \infty$  is taken keeping  $\epsilon$  fixed. Equation (5.15) leads to an  $A^{(2)}$  of the form given in Eq. (5.8). From the relation given in Eq. (5.6) it then follows that  $\underline{A}_n$  is of the form of Eq. (5.5) with the  $n$  particle master operator given as a sum of 1 particle transition rates. The results of Paper I are thus directly applicable to the system of interacting oscillators. The eigenfunctions and eigenvalues of this one particle transition rate matrix  $A_1(a_1, \gamma_1)$  can be found in the paper by Montroll and Shuler.<sup>(8)</sup>

The results of this section can be briefly summarized as follows. If the transition rate matrix  $\underline{A}_N$  for the  $N$ -particle master equation can be written

in the form of Eq. (5.1), which is the case, for instance, for systems with weak interactions and short range forces, and if the operator  $\underline{A}_N$  is of the form given in Eq. (2.23), i.e. if the  $N$ -particle master equation reduces to an  $n$ -particle master equation by summation over the other  $N-n$  particles, then in the thermodynamic limit,  $\underline{A}_N$  reduces to a sum of 1-particle transition rates  $\underline{A}_1$ . This implies that for all such systems

$$\underline{U}_n(t) - \underline{U}_n^{(0)} \sim \left[ \underline{P}_1(t) - \underline{P}_1^{(0)} \right]^n \quad (5.19)$$

$$\underline{P}_n(t) - \underline{P}_n^{(0)} \sim \left[ \underline{P}_1(t) - \underline{P}_1^{(0)} \right] \quad (5.20).$$

These results are identical with those obtained by us in 1 for systems described by independent particle dynamics which are also characterized by 1-particle transition rates  $\underline{A}_1$ .

REFERENCES

1. I. Oppenheim, K. E. Shuler and G. H. Weiss, *J. Chem. Phys.* 46, 4100 (1967).
2. I. Oppenheim, K. E. Shuler and G. H. Weiss, *J. Chem. Phys.* 50, 3662 (1969).
3. D. Bedaux, K. E. Shuler and I. Oppenheim, *J. Stat. Phys.* 2, 1 (1970).
4. The term "relaxant" has been suggested to us by Professor Michael E. Fisher as a generic term for functions which are useful in studying the decay of correlations.
5. R. Glauber, *J. Math. Phys.* 4, 294 (1963).
6. K. E. Shuler, *Phys. Fluids* 2, 442 (1959).
7. K. E. Shuler, *J. Chem. Phys.* 32, 1692 (1960).
8. E. W. Montroll and K. E. Shuler, *J. Chem. Phys.* 26, 454 (1957).